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(54) A catalytic conversion process for producing isobutane and isoparaffin-enriched gasoline

(57) A process for catalytic conversion of hydrocarbon feedstock to produce isobutane and isoparaffin-enriched gasoline which comprises two different reactions, the preheated feedstock is contacted with hot regenerated catalyst in the lower part of a reactor with the result that catalytic cracking reaction takes place, and the mixture of vapors and the coke deposited catalyst are up-flowed and enter into a suitable reaction environment with the result that isomerization and hydrogen transfer reaction take place. The produced LPG has an isobutane content of about 20wt% to about 40wt% and the produced gasoline contains isoparaffin content of about 30wt% to about 45wt% and olefin content of less than 30wt%. RON and MON of the gasoline are 90-93 and 80-84 respectively.

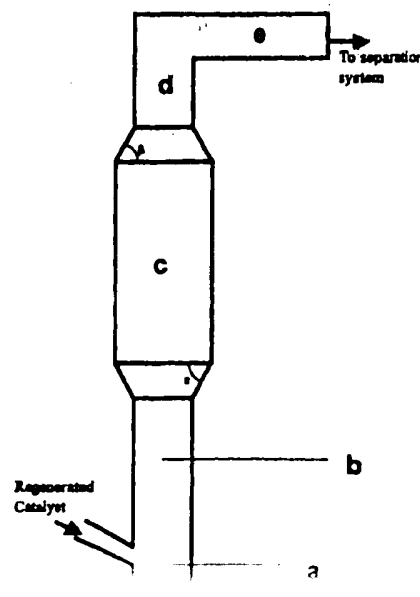


FIG. 1

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## Description

## Background of the Invention

5 [0001] This invention relates to a process for catalytic conversion of hydrocarbon feedstock in the absence of added hydrogen. More particularly, the present invention relates to a catalytic conversion process for producing isobutane and isoparaffin-enriched gasoline.

[0002] The mixture of isoparaffins possessing high octane number, low octane sensitivity, appropriate volatility and clean burning is an ideal blending components for aviation gasoline and motor gasoline. The mixture of isoparaffins can be obtained by propylene polymerization or alkylation reaction of isobutane and olefins.

10 [0003] The conventional fluidized catalytic cracking (FCC) technology is used for producing gasoline with a yield of up to 50wt%. In the 1980s, the phase down of leaded gasoline forced the catalytic cracking technology to go forward to the production of high octane gasoline. The changing market demands have resulted in a great change in technology and catalyst types. The advance in technological development is to increase reaction temperature, shorten reaction time, intensify reaction severity, suppress hydrogen transfer reaction and overcracking reaction and improve the contacting efficiency between feedstock and hot catalyst at the bottom of a riser reactor. In catalyst development, the catalysts containing USY zeolite supported on an inert or active matrix or containing different typed zeolites have been put into commercial use.

20 [0004] Though FCC technology has been advanced to meet octane blending requirement, whether it is by means of changing in process parameters or using novel catalysts for increasing gasoline octane number, it results in an increase in olefin content of FCC gasoline. Apparently, there is a great difference between the olefin contents of about 35wt%~65wt% in FCC gasoline and that required for reformulated gasoline (RFG). FCC liquid petroleum gas (LPG) has an olefin content of up to 70wt%, in which butylenes is several times as much as the yield of isobutane, so it is not fit to be used as feedstock for alkylation.

25 [0005] USP5,154,818 discloses a method for the fluidized catalytic cracking of plural hydrocarbon feedstocks in a riser reactor to produce more gasolines of high octane number. The process generally comprises two reaction zones. A relatively light hydrocarbon feedstock contacts with spent catalyst in a first reaction zone located in the bottom of conventional riser where aromatization and oligomerization take place. All of the first reaction zone effluent, the regenerated catalyst and heavy hydrocarbon feedstock are introduced into the second reaction zone where heavy hydrocarbon feedstock is cracked to desired reaction products. The reaction products and spent catalyst then pass through disengager for removal of entrained catalyst before the hydrocarbon vapors pass into a separation system. Spent catalyst passes into stripper and is divided into two parts, one is introduced into regenerator for burning off coke, the other part is recycled to the first reaction zone.

35 [0006] USP4,090,948 discloses a catalytic cracking process for producing the desired conversion of hydrocarbon feedstock of inferior quality (having higher contents of basic nitrogen and carbon residue) to obtain higher yields of the desired products in a riser reactor. The process generally comprises contacting the hydrocarbon feedstock containing the highly reactive nitrogen and carbon residue with a recycled spent catalyst in the first reaction zone where the highly reactive nitrogen and carbon residue will deposit on the spent catalyst and then contacting the resultant mixture with freshly regenerated catalyst in the second reaction zone. The reaction products and spent catalyst then pass through disengager for removal of entrained catalyst before the hydrocarbon vapors pass into a separation system. Spent catalyst passes into stripper and is divided into two parts, one is introduced into regenerator for burning off coke and then returned to the second reaction zone, and the other part is recycled without regeneration to the first reaction zone.

40 [0007] Though the above two prior art processes have divided an iso-diameter riser reactor into two reaction zones, the reactions take place at lower temperature in the first reaction zone and the reactions take place at higher temperature in the second reaction zone. In addition, the processes utilize a conventional riser reactor without flexibility for adjusting operating conditions. This arrangement is subject to significant disadvantages to carry on catalytic cracking reaction and selective hydrogen transfer at the same time for producing LPG with higher yield of isobutane and isoparaffin enriched gasoline.

45 [0008] An object of the present invention is to provide a catalytic conversion process for producing isobutane and isoparaffin-enriched gasoline to meet the requirement for blending components of the RFG, i.e. limiting the olefin content on the premise of maintaining higher gasoline octane number.

## Summary of the Invention

55 [0009] The process provided by the present invention is to contact the preheated hydrocarbon feedstock with hot regenerated catalyst in the lower part of a reactor with the result that hydrocarbon cracking reaction takes place at higher reaction temperature and shorter reaction time, and then the resultant mixture is up-flowed and enters into a suitable reaction environment with the result that isomerization and hydrogen transfer reaction take place at lower reaction

temperature and longer reaction time. The reaction products and spent catalyst then pass through disengager for removal of entrained catalyst. The reaction products flow into subsequent separation system. Spent catalyst is shipped with steam, and then flow into the regenerator for regeneration, and thereafter the hot regenerated catalyst is recycled to the lower part of the reactor.

5 [0010] The process provided by the present invention employs a reactor to carry on two different reactions under different operating conditions, said reactor is preferably selected from the group consisting of an iso-diameter riser, an iso-linear velocity riser, a multi-cascade riser, a fluidized bed or a combination reactor of an iso-diameter riser and a fluidized bed.

[0011] The applicants have found that the olefins produced by catalytic cracking reaction can be selectively converted into isoparaffins and aromatics or isoparaffins and coke under specific reaction conditions and with specific catalysts.

[0012] The present invention is practiced by different embodiments. In embodiment one, the invention is a process comprising: the preheated hydrocarbon feedstock is atomized with injection steam and charged into the bottom of a conventional iso-diameter riser, and then mixed with hot regenerated catalyst with the result that feedstock is vaporized and cracked. The product vapors and the coke deposited catalyst are up-flowed and are mixed with cooled regenerated catalyst with the result that isomerization and hydrogen transfer reaction take place. The reaction vapors and catalyst flow into disengager where entrained catalyst is separated and dropped into the catalyst stripper. The reaction vapors are separated into products in subsequent separation system. Spent catalyst is stripped and introduced into regenerator for regeneration. Regenerated catalyst is divided into two parts, one is recycled into the prelift zone of the riser, and the other part is cooled in catalyst cooler and then recycled into the second reaction zone.

[0013] In embodiment two, this invention is a process comprising: the preheated hydrocarbon feedstock is atomized with injection steam and charged into the bottom of a conventional iso-diameter riser, and then mixed with hot regenerated catalyst with the result that the feedstock is vaporized and cracked. The product vapors and the coke deposited catalyst are up-flowed and are mixed with cooled semi-regenerated catalyst with the result that isomerization and hydrogen transfer reaction take place. The reaction vapors and catalyst flow into disengager where entrained catalyst is separated and dropped into the catalyst stripper. The reaction vapors are separated into products in subsequent separation system. Spent catalyst is stripped and introduced into the primary regenerator for regeneration. Semi-regenerated catalyst is divided into two parts, one flows into the secondary regenerator for regeneration, and then is recycled into the prelift zone of the riser, and the other part is cooled in catalyst cooler and then recycled into the second reaction zone.

[0014] In embodiment three, this invention is a process comprising: the preheated hydrocarbon feedstock is atomized with injection steam and charged into the bottom of the riser in a combination reactor or an iso-diameter riser and a fluidized bed, and then mixed with hot regenerated catalyst with the result that the feedstock is vaporized and cracked. The product vapors and the coke deposited catalyst in the riser flow upward and are mixed with cooled regenerated catalyst with the result that isomerization and hydrogen transfer reaction take place in the fluidized bed. The reaction vapors and catalyst flow into disengager where entrained catalyst is separated and dropped into the catalyst stripper. The reaction vapors are separated into products in subsequent separation system. Spent catalyst is stripped and introduced into regenerator for regeneration. Regenerated catalyst is divided into two parts, one is recycled into the prelift zone of the riser, and the other part is cooled in catalyst cooler and then recycled into the fluidized bed.

[0015] In a more preferred embodiment of this invention, this invention comprises that the preheated hydrocarbon feedstock is atomized with injection steam and charged into the bottom of the first reaction zone in a multi-cascade riser, and then mixed with hot regenerated large particle size distribution catalyst containing USY zeolite with the result that feedstock is vaporized and cracked, providing the lifting force to carry the product vapors and the coke deposited catalyst in the first reaction zone into the second reaction zone where the effluents are mixed with the cooled regenerated small particle size distribution catalyst containing rare-earth Y zeolite with the result that isomerization and hydrogen transfer reaction take place. The reaction vapors and catalyst flow into disengager where entrained catalyst is separated and dropped into the catalyst stripper. The reaction vapors are separated into products in subsequent separation system. Spent catalyst is stripped and introduced into regenerator for regeneration. Regenerated catalyst is divided into the large particle size distribution catalyst and the small particle size distribution catalyst, the large particle size distribution catalyst is recycled into the prelift zone of the riser, and the small particle size distribution catalyst is cooled in catalyst cooler and then recycled into the second reaction zone.

[0016] The above embodiments are not meant to limit the present invention to the details disclosed herein.

#### Brief Description of the Drawings

[0017]

invention, comprising prelift zone a, the first reaction zone b, the second reaction zone c, outlet zone d, and horizontal tube e

Fig.2 shows the more preferred schematic flow diagram used for carrying out this invention, comprising conduits 1, 3, 4, 6, 11, 13, 17 and 18, prelift zone 2, the first reaction zone 5, the second reaction zone 7, outlet zone 8, disengager 9, cyclone 10, stripper 12, solvent catalyst standpipe 14, regenerator 15, and regenerated catalyst standpipe 16.

### Detailed Description of the Invention

[0018] The process of the present invention comprises the steps as follows:

1. The preheated hydrocarbon feedstock is charged to the bottom of a reactor and contacted with hot regenerated catalyst with the result that they are vaporized and cracked. Catalytic cracking reaction temperature is preferably from about 530 °C to about 620 °C, and even more preferably from about 550 °C to about 600 °C the reaction time is preferably from about 0.5 second to about 2 seconds, and even more preferably from about 0.8 second to about 1.5 seconds, the weight ratio of catalyst to feed (hereinafter referred to as C/O ratio) is preferably from about 3:1 to about 15:1, and even more preferably from about 4:1 to about 12:1.

2. The product vapors and the coke deposited catalyst are up-flowed and enter into a suitable reaction environment with the result that isomerization and hydrogen transfer reaction take place. The reaction temperature is preferably from about 420 °C to about 550 °C, and even more preferably from about 460 °C to about 510 °C, the reaction time is preferably from about 2 seconds to about 30 seconds, and even more preferably from about 3 seconds to about 15 seconds the C/O ratio is preferably from about 3:1 to about 18:1, and even more preferably from about 4:1 to about 15:1. The weight ratio of steam to feed (hereinafter referred to as S/O ratio) is preferably from about 0.03:1 to about 0.3:1, and even more preferably from about 0.05:1 to about 0.3:1, and the reaction pressure is preferably about 130kPa to 450kPa in reaction zone.

3. Product vapors are separated into LPG with high yield of isobutane, isoparaffin enriched gasoline and other products. Spent catalyst is dropped into the catalyst stripper and then introduced to regenerator for regeneration, and thereafter the hot regenerated catalyst is recycled into the first reaction zone.

[0019] The process provided by the present invention employs a reactor to carry on two different reactions under different operating conditions; it is preferably selected from the group consisting of an iso-diameter riser, an iso-linear velocity riser, a multi-cascade riser, a fluidized bed or a combination of an iso-diameter riser and a fluidized bed.

[0020] When the process of the present invention is carried out in an iso-diameter riser reactor which is same as a conventional riser reactor used in a refinery or an iso-linear velocity riser reactor in which the velocity of fluid is approximately even or a fluidized bed reactor, The iso-diameter riser or iso-linear velocity riser is divided into a prelift zone, a first reaction zone, a second reaction zone from bottom to top while the fluidized bed reactor comprises only a first reaction zone and a second reaction zone. The height ratio of the first reaction zone to the second reaction zone is 10~40:90~60. One inlet or multi-inlets of quenching mediums is set up at the bottom of the second reaction zone, and/or a heat remover having a height of about 50%~90% of that of the second reaction zone is located in the second reaction zone for adjusting the reaction temperature and time in the reaction zone. As the term used herein, said quenching medium is generally one or more selected from the group consisting of quenching liquids, cooled regenerated catalyst cooled semi-regenerated catalyst or fresh catalyst or the mixtures thereof, in which quenching liquid is preferably selected from the group consisting of LPG, naphtha, stabilized gasoline, light cycle oil (LCO), heavy cycle oil (HCO) or water or the mixtures thereof. LPG, naphtha and gasoline having high olefin content can not only act as quenching mediums, but also participate in reaction. The cooled regenerated and semi-regenerated catalysts are obtained by cooling catalyst through catalyst cooler after the primary stage and secondary stage regeneration respectively. As the terms used herein, said regenerated catalyst refers to catalyst that has a residual carbon content of below 0.1 wt%, more preferably below about 0.05wt%, and said semi-regenerated catalyst refers to catalyst that has a residual carbon content of from about 0.1 wt% to about 0.9wt%, more preferably from about 0.15wt% to about 0.7wt%.

[0021] When the process of the present invention is carried out in a combination reactor of an iso-diameter riser and a fluidized bed, wherein the lower iso-diameter riser refers to the first reaction zone, the upper fluidized bed refers to the second reaction zone. One inlet or multi-inlets of quenching mediums is set up at the bottom of the second reaction zone and/or a heat remover having a height of about 50%~90% of that of the second reaction zone is located in the second reaction zone for adjusting the reaction temperature and time in the reaction zone. As the term used herein, said quenching medium is generally one or more selected from the group consisting of quenching liquid, cooled regenerated catalyst, cooled semi-regenerated catalyst or fresh catalyst or the mixtures thereof, in which quenching liquid is preferably selected from the group consisting of LPG, naphtha, stabilized gasoline, light cycle oil (LCO), heavy cycle oil (HCO) or water or the mixtures thereof. LPG, naphtha and gasoline having high olefin content can not only act as

quenching mediums, but also participate in reaction. The cooled regenerated and semi-regenerated catalysts are obtained by cooling catalyst through catalyst cooler after the primary stage and secondary stage regeneration respectively. As the terms used herein, said regenerated catalyst refers to catalyst that has a residual carbon content of below 0.1 wt%, more preferably below about 0.05wt%, said semi-regenerated catalyst refers to catalyst that has a residual carbon content of from about 0.1 wt% to about 0.9wt%, more preferably from about 0.15wt% to about 0.7wt%.

[0022] When the process of the present invention is carried out in a multi-cascade riser reactor, of which the structural features are shown in FIG. 1, the riser consists of a prelift zone a, a first reaction zone b, a second reaction zone with enlarged diameter c, the outlet zone with reduced diameter d from bottom to top along the coaxial direction. The end of outlet zone is connected to a horizontal tube e. The conjunct section between the first reaction zone and the second reaction zone is a circular truncated cone whose vertical section isotrapezia vertex angle  $\alpha$  is generally about  $30^\circ \sim 80^\circ$ . The conjunct section between the second reaction zone and the outlet zone is a circular truncated cone whose vertical section isotrapezia base angle  $\beta$  is generally about  $45^\circ \sim 85^\circ$ .

[0023] The total height of the riser is generally from about 10 meters to about 60 meters. The diameter of the prelift zone is the same as that of a conventional iso-diameter riser and generally from about 0.02 meter to about 5 meters. The height of the prelift zone is about 5%~10% of the total height of the riser. The function of this zone is to lift regenerated catalyst upward and to improve initial feed and catalyst contacting with the aid of a prelift medium that is selected from steam or dry gas same as that used in a conventional iso-diameter riser reactor.

[0024] The structure of the first reaction zone of the riser is similar to the lower section of a conventional iso-diameter riser. Its diameter is equal to or greater than that of the prelift zone. The diameter ratio of the former to the latter is generally from about 1:1 to about 2:1. The height of the first reaction zone is about 10%~30% of the total height of the riser. The preheated feedstocks are atomized with injection steam and charged into this section, and then mixed with hot regenerated catalyst with result that cracking reaction takes place at higher reaction temperature and C/O ratio and shorter reaction time.

[0025] The diameter of the second reaction zone is greater than that of the first reaction zone. The diameter ratio of the former to the latter is generally from about 1.5:1 to about 5:1. The height of the second reaction zone is about 30~60% of the total height of the riser. The function of this zone is to reduce the velocity of vapors and catalyst and the reaction temperature in order to suppress cracking reaction and increase isomerization reaction and hydrogen transfer reaction. The method of controlling the second reaction temperature is to inject quenching mediums at the conjunct section between the first reaction zone and the second reaction zone and/or to install a heat remover in the zone. The height of the heat remover is generally from about 50% to about 90% of that of the second reaction zone. The zone temperature is generally from about  $420^\circ\text{C}$  to about  $550^\circ\text{C}$ . The contacting time of vapor and catalyst is generally from about 2 seconds to about 30 seconds. As the term used herein, said quenching medium is generally one or more selected from the group consisting of quenching liquids cooled regenerated catalyst, cooled semi-regenerated catalyst or fresh catalyst or the mixtures thereof, in which quenching liquid is preferably selected from the group consisting of LPG, naphtha, stabilized gasoline, light cycle oil (LCO), heavy cycle oil (HCO) or water or the mixtures thereof. LPG, naphtha and gasoline having high olefin content can not only act as quenching mediums, but also participate in reaction. The cooled regenerated and semi-regenerated catalysts are obtained by cooling catalyst through catalyst cooler after the primary stage and secondary stage regeneration respectively. As the terms used herein, said regenerated catalyst refers to catalyst that has a residual carbon content of below 0.1 wt%, more preferably below about 0.05wt%, and said semi-regenerated catalyst refers to catalyst that has a residual carbon content of from about 0.1 wt% to about 0.9wt%, more preferably from about 0.15wt% to about 0.7wt%.

[0026] The structure of the outlet zone is similar to that of a conventional iso-diameter riser. The diameter ratio of the outlet zone to the first reaction zone is generally about 0.8:1 to about 1.5:1. The height of this zone is generally about 0~20% of total height of the riser. The function of this zone is to increase effluent velocity and to suppress over-cracking reaction.

[0027] One end of the horizontal tube is connected to the outlet zone and the other end is connected to the disengager. When the height of the outlet zone is equal to zero, one end of the horizontal tube is connected to the second reaction zone and the other end is connected to the disengager. The function of the horizontal tube is to link the outlet zone with the disengager.

[0028] Feedstocks suitable for the process of the present invention include distillate having different boiling ranges, residue and crude. More specifically, the feedstocks are selected from the group consisting of atmospheric gas oil, naphtha, catalytic gasoline, diesel, vacuum gas oil (VGO), atmospheric residue (AR) or vacuum residue (VR), coker gas oil (CGO), deasphalted oil (DAO), hydrotreated residue, hydrocracked residue, shale oil or the mixtures thereof.

[0029] The processes of the present invention are adaptable for use with all known catalyst types, including amorphous silica-alumina catalysts and zeolite catalysts with the active components preferably selected from the group consisting of Y, HY, USY or ZSM-5 series or any other zeolites typically employed in the cracking of hydrocarbons with or without rare earth and/or phosphor or the mixtures thereof.

type catalysts, including large and small particle size distribution catalysts or high and low apparent bulk density catalysts with the active components preferably selected from the group consisting of Y, HY, USY or ZSM-5 series or any other zeolites typically employed in the cracking of hydrocarbons with or without rare earth and/or phosphor or mixtures thereof. Large and small particle size distribution catalysts or high and low apparent bulk density catalysts flow into different reaction zone respectively. For example, the large particle size distribution catalyst with USY zeolite flows into the first reaction zone for increasing cracking reaction, while the small particle size distribution catalyst with rare earth Y zeolite flows into the second reaction zone for increasing hydrogen transfer reaction. The mixed large and small particle size distribution catalysts are stripped in a stripper and are combusted in a regenerator, and then are separated into large particle size distribution catalyst and small particle size distribution catalyst. The large and small particle size distribution catalyst are partitioned within the range of about 30~40  $\mu\text{m}$ . The high and low apparent bulk density catalyst are partitioned within the range of about 0.6~0.7  $\text{g/cm}^3$ .

[0031] The present invention has several important advantages in that:

1. When the present invention is carried out in a conventional iso-diameter riser or a fluidized bed reactor, the object of this invention is obtained by reducing throughput capacity and controlling low reaction temperature.
2. The multi-cascade riser reactor used in the present invention has advantages in that the cracking reaction at the bottom of the riser take place at higher reaction temperature and C/O ratio, meanwhile, overcracking reaction and thermal reaction are suppressed at the top of the riser, while isomerization and hydrogen transfer reaction take place in the middle section of the riser at lower reaction temperature and longer reaction time.
3. The process provided by the present invention produces LPG having an isobutane content of about 20~40wt% and gasoline having an isoparaffin content of about 30~45wt%, and olefin content of below 30wt%, whereas the conventional iso-diameter riser catalytic cracking produces LPG having an isobutane content of below 10wt% and gasoline having an isoparaffin content of below 20wt%, and olefin content of above 40wt%.
4. The process of the present invention is adaptable for different hydrocarbon feedstocks and different type catalysts.

[0032] The following description of the more preferable practicing mode is more fully explained in the context of attached Fig.2.

[0033] Fig.2 shows the schematic flow diagram used to produce isobutane and isoparaffin enriched gasoline in a multi-cascade riser. The shape and size of the apparatus and pipelines are not limited in the attached diagram but depend on specific embodiments.

[0034] The prelift steam is introduced into prelift zone 2 via conduit 1. Hot regenerated catalyst flow into prelift zone 2 via regenerated catalyst standpipe 16 and is lifted by prelift steam. The preheated feedstock via conduit 4 is mixed with atomized steam via conduit 3 in proportion to form a mixture. The mixture is charged into prelift zone, and then is contacted with hot regenerated catalyst, flowing into the first reaction zone 5 where cracking reaction takes place under certain reaction conditions. The effluent is mixed with quenching mediums via conduit 6, flowing into the second reaction zone 7 with the result that isomerization and hydrogen transfer reaction take place under certain reaction conditions. The reacted effluent flows into outlet zone 8 where the effluent is accelerated, and then passes through disengager 9, where entrained catalyst is separated and dropped into the catalyst stripper 12. Residual catalyst is separated from the reaction vapors in a set of cyclones 10 located in the upper section of the reactor. The reaction vapors pass to subsequent separation system via conduit 11. Spent catalyst is contacted with stripping steam via conduit 13 to remove heavy hydrocarbons on the catalyst. After steam stripping, the catalyst flows to the spent catalyst standpipe 14 to the regenerator 15, where the spent catalyst is contacted with air via conduit 17 with the result that catalyst regeneration takes place to burn off coke. Flue gas is discharged from the regenerator via conduit 18. The hot regenerated catalyst is recycled into the bottom of the riser via regenerated catalyst standpipe 16.

#### Examples

[0035] The following examples are used to demonstrate the efficacy of the present invention and are not meant to limit the scope of the invention to the detail examples shown herein. The properties of the feedstocks and catalysts used in practical examples and comparative examples are listed in tables 1 and 2 respectively. The catalysts listed in table 2 are manufactured by the catalyst complex of Qilu Petrochemical Corporation, SINOPEC.

#### Example 1

[0036] The example showed that hydrocarbon feedstock was converted to produce isobutane and isoparaffin enriched gasoline in a conventional pilot plant iso-diameter riser in accordance with the present invention.

[0037] The preheated hydrocarbon feedstock D listed in table 1 was charged into the riser and contacted with hot

regenerated catalyst D listed in table 2 in the presence of steam with the result that some reactions took place. The reaction products were separated into isobutane enriched LPG, isoparaffin enriched gasoline and other products. Spent catalyst flowed into regenerator via stripping. After regeneration, the regenerated catalyst was recycled for use.

- 5 [0038] Operating conditions and product slate were listed in table 3. Gasoline properties were listed in table 4. Table 3 showed that 20.72wt% of LPG was isobutane. Table 4 showed that the gasoline had an isoparaffin content of 31.92wt%, whereas olefin content was 29.32wt%.

#### Comparative example 1

- 10 [0039] Compared with example 1, the reaction time reduced from 5.5 seconds to 3.5 seconds, while other operating conditions were similar in the example. Operating conditions and product slate were listed in table 3. Gasoline properties were listed in table 4. Table 3 showed that 8.95wt% of LPG was isobutane. Table 4 showed that the gasoline had an isoparaffin content of 22.06wt%, and an olefin content of 47.65wt%.

#### 15 Example 2

[0040] The example showed that hydrocarbon feedstock was converted to produce isobutane and isoparaffin enriched gasoline in a combination reactor of an iso-diameter riser and a fluidized bed in accordance with the present invention,

- 20 [0041] The preheated hydrocarbon feedstock D listed in table 1 was charged into the riser and contacted with hot regenerated catalyst D listed in table 2 in the presence of steam with the result that some reactions took place. The reaction products were separated into isobutane enriched LPG, isoparaffin enriched gasoline and other products. Spent catalyst flowed into regenerator via stripping. After regeneration, regenerated catalyst was recycled for use.

- 25 [0042] Operating conditions, product slate and gasoline properties were listed in table 5. Table 5 showed that 32.04wt% of LPG was propylene, 23.20wt% of LPG was isobutane, and that the gasoline had an isoparaffin content of 30.16wt%, and an olefin content of 28.63wt%.

#### Comparative example 2

- 30 [0043] The Comparative example was conducted in a conventional pilot plant iso-diameter riser reactor. The catalyst and feedstock used were the same as that in example 2. Operating conditions, product slate and gasoline properties were listed in table 5. Table 5 showed that 32.80wt% of LPG was propylene, 7.76wt% of LPG was isobutane, and that the gasoline had an isoparaffin content of 17.30wt%, and an olefin content of 45.30wt%.

#### 35 Example 3

[0044] The example showed that hydrocarbon feedstock was converted to produce isobutane and isoparaffin enriched gasoline in a multi-cascade riser reactor in accordance with the present invention.

- 40 [0045] The total height of the multi-cascade riser is 15 meters in which the height of the prelift zone with a diameter of 0.025 meter is 1.5 meters, the height of the first reaction zone with a diameter of 0.025 meter is 4 meters, the height of the second reaction zone with a diameter of 0.1 meter is 6.5 meters, and the height of the outlet zone with a diameter of 0.025 meter is 3 meters. The isotrapezia vertex angle  $\alpha$  of the vertical section of the conjunct section between the first reaction zone and the second reaction zone is about 45°, and the isotrapezia base angle  $\beta$  of the vertical section of the conjunct section between the second reaction zone and the outlet zone is about 60°.

- 45 [0046] The preheated hydrocarbon feedstock B listed in table 1 was charged into the riser and contacted with hot regenerated catalyst C listed in table 2 in the presence of steam with the result that some reactions took place. The reaction products were separated into isobutane enriched LPG, isoparaffin enriched gasoline and other products. Spent catalyst flowed into regenerator via stripping. After regeneration, regenerated catalyst was recycled for use.

- 50 [0047] Operating conditions and product slate were listed in table 6. Gasoline properties were listed in table 7. Table 6 showed that 35.07wt% of LPG was isobutane. Table 7 showed that the gasoline had an isoparaffin content of 36.0wt%, whereas olefin content was 28.11 wt%.

#### Comparative example 3

- 55 [0048] The comparative example was conducted in a conventional pilot plant iso-diameter riser reactor. The catalyst and feedstock used were the same as that in example 3. Operating conditions and product slate were listed in table 6. Gasoline properties were listed in table 7. Table 6 showed that 15.74wt% of LPG was isobutane. Table 7 showed that the gasoline had an isoparaffin content of 17.30wt%, and an olefin content of 45.30wt%.

## Example 4

[0049] The example showed that hydrocarbon feedstock was converted to produce isobutane and Isoparaffin enriched gasoline over different type catalysts in a pilot plant multi-cascade riser reactor in accordance with the present invention.

[0050] The reactor used in the example was the same as that in example 3. The feedstocks used were the mixture of 80wt% of VGO A and 20wt% of CGO C, and AR D, whose properties were listed in table 1. Operating conditions, catalyst types, product slate and Gasoline properties were listed in table 8. Table 8 showed that about 28~32wt% of LPG was isobutane, and the gasoline had an isoparaffin content of about 33~39wt% and an olefin content of 16.0~27.0wt%.

## Example 5

[0051] The example showed that hydrocarbon feedstock was converted to produce isobutane and Isoparaffin enriched gasoline in a pilot plant multi-cascade riser reactor wherein gasoline with higher olefin content acted as quenching medium in accordance with the present invention.

[0052] The reactor, catalyst and feedstock were the same as those used in example 3. The gasoline with higher olefin content acting as quenching medium was that obtained in comparative example 3. The gasoline was injected into the bottom of the second reaction zone, other operating conditions were similar to these of example 2.

[0053] Operating conditions and product slate were listed in table 9. Gasoline properties were listed in table 10. Table 9 showed that 34.15wt% of LPG was isobutane. Table 10 showed that the gasoline had an isoparaffin content of 43.86wt%, and an olefin content of 20.51wt%.

## Example 6

[0054] The example showed that hydrocarbon feedstock was converted to produce isobutane and isoparaffin enriched gasoline in a pilot plant multi-cascade riser reactor in accordance with the present invention.

[0055] The total height of the multi-cascade riser is 15 meters in which the height of the prelift zone with a diameter of 0.025 meter is 1.5 meters, the height of the first reaction zone with a diameter of 0.025 meter is 4.5 meters, and the height of the second reaction zone with a diameter of 0.05 meter is 9 meters. The isotrapezia vertex angle  $\alpha$  of the vertical section of the conjunct section between the first reaction zone and the second reaction zone is about 45°.

[0056] The catalyst and feedstock used were the same as those used in example 3. Operating conditions and product slate were listed in table 9. Gasoline properties were listed in table 10. Table 9 showed that 32.91wt% of LPG was isobutane. Table 10 showed that the gasoline had an isoparaffin content of 33.31 wt%, whereas olefin content was 26.51wt%.

## Example 7

[0057] The example showed that hydrocarbon feedstock was converted to produce isobutane and Isoparaffin enriched gasoline in a pilot plant multi-cascade riser reactor in accordance with the present invention.

[0058] The reactor used was the same as that in example 3. The preheated hydrocarbon feedstock E listed in table 1 was charged into the first reaction zone and contacted with hot regenerated catalyst C listed in table 2 in the presence of steam with the result that cracking reaction took place, then the resultant mixture flowing into the second reaction zone was mixed with cooled regenerated catalyst via cooler. The reaction products were separated into isobutane enriched LPG, isoparaffin enriched gasoline and other products. Spent catalyst flowed into regenerator via stripping. After regeneration, the regenerated catalyst was divided into two parts. one was returned into the bottom of the first reaction zone, and the other part was cooled in catalyst cooler and recycled into the bottom of the second reaction zone for use.

[0059] Operating conditions, catalyst types, product slate and gasoline properties were listed in table 11. Table 11 showed that LPG had an isobutane content of about 35.49wt%, whereas butylenes content was about 19.62wt%, and that the gasoline had an isoparaffin content of about 35.02wt%, and an olefin content of 26.43wt%.

## Comparative example 4

[0060] Compared with example 7, the process was operated in the same manner, except that the selected quenching medium injected into the second reaction zone was naphtha instead of the cooled regenerated catalyst.

[0061] Operating conditions, catalyst types, product slate and gasoline properties were listed in table 11. Table 11 showed that LPG had an isobutane content of about 26.53wt%, whereas butylenes content was about 21.91wt%, and



that the gasoline had an isoparaffin content of about 30.92wt%, whereas olefin content was 30.22wt%.

#### Example 8

5 [0062] The example showed that hydrocarbon feedstock was converted to produce isobutane and isoparaffin enriched gasoline in a pilot plant multi-cascade riser reactor in accordance with the present invention.

[0063] Compared with example 7, the process was operated in the same manner, except that the selected prelift medium for prelifting the cooled regenerated catalyst used as quenching medium was naphtha instead of steam.

10 [0064] Operating conditions, catalyst types, product slate and gasoline properties were listed in table 11. Table 11 showed that LPG had an isobutane content of about 36.03wt%, whereas butylenes content was 19.50wt%, and that the gasoline had an isoparaffin content of about 37.74wt%, and an olefin content of 23.78wt%.

Table 1

Feedstock No.	A	B	C	D	E
Feedstock Name	VGO	VGO	CGO	AR	VR
Density(20°C), kg/m <sup>3</sup>	873.0	890.5	869.6	897.4	920.9
Viscosity, mm <sup>2</sup> /s					
80°C	13.01	7.93	6.66	54.20	
100°C	8.04	5.08	4.54	30.02	114.4
Carbon Residue, wt%	0.15	0.7	0.84	4.5	8.2
Pour Point, °C	50	40	33	47	25
Basic nitrogen, ppm	340		1920		
Nitrogen, wt%	0.10	0.16	0.29	0.27	0.33
Sulfur, wt%	0.073	0.53	0.13	0.14	0.21
Carbon, wt%	86.5	85.00	86.55	86.26	86.91
Hydrogen, wt%	13.24	12.62	13.03	12.81	12.55
Metal content, ppm					
Ni	<0.1	0.16	0.70	5.2	8.8
V	<0.1	0.15	<0.1	<0.1	0.1
Fe	54	-	0.80	4.2	1.8
Cu	<0.1	-	<0.1	<0.1	<0.1
Na	-	0.45		5.5	3.0
Distillation, °C					
IBP	346	242	238	324	415
10%	411	322	328	408	545
30%	437	380	363	486	-
50%	462	410	382	-	-
70%	489	437	409	-	-
90%	523	480	429	-	-
EP	546	516	-	-	-

Table 2

Catalyst No.	A	B	C	D
Trade mark	CRC-1	RHZ-200	ZCM-7	RAG-1
Zeolite types	REY	REHY	USY	REY-USY-ZRP
Chemical Composition, wt%				
Aluminum oxide	26.5	33.0	46.4	44.6
Sodium oxide	0.19	0.29	0.22	0.13
Ferric oxide	0.09	1.1	0.32	
Apparent Bulk Density, Kg/m <sup>3</sup>	450	560	690	620
Pore Volume, ml/g	0.41	0.25	0.38	0.36
Surface area, m <sup>2</sup> /g	132	92	164	232
Attrition index, wt%hr <sup>-1</sup>	4.2	3.2	-	2.5
Particle size distribution, wt%				
0~40 µm	7.3	15.2	4.8	13.1
40~80 µm	43.7	55.1	47.9	54.9
>80 µm	44.3	27.3	47.3	32.0

Table 3

	Example 1	Comparative Example 1
Reaction Temperature, °C		530
The first reaction zone	550	-
The second reaction zone	510	-
Reaction time, second	5.5	3.5
The first reaction zone	2.0	-
The second reaction zone	3.5	-
C/O	7.82	6.7
S/O	0.1	0.1
Product slate, wt%		
Dry gas	3.25	3.75
LPG	25.34	26.02
In which isobutane	5.25	2.33
Gasoline	47.34	46.55
LCO	10.32	10.10
HCO	5.95	5.25
Coke	7.40	7.86
Loss	0.40	0.47

Table 4

	Example 1	Comparative Example 1
Density(20°C), Kg/m <sup>3</sup>	729.8	711.3
Octane Number		
RON	91.6	92.1
MON	80.7	80.5
Induction period, min	695	535
Existent Gum, mg/100ml	6	2
Sulfur, wt%	0.031	0.028
Nitrogen, wt%	0.0068	0.0041
C, wt%	86.65	85.98
H, wt%	13.34	13.86
Distillation, °C		
IBP	47	41
10%	61	54
30%	74	65
50%	97	86
70%	131	119
90%	173	160
EP	206	192
Composition, wt%		
Paraffins	36.42	26.94
n-paraffins	4.50	4.88
Iso-paraffins	31.92	22.06
Naphthene	7.32	7.16
Olefins	29.32	47.65
Aromatics	26.94	18.25

Table 5

	Example 2	Comparative Example 2
Reactor	Convention riser plus fluidized bed	Convention riser
Reaction Temperature, °C		530
The first reaction zone	550	-
The second reaction zone	500	-
C/O	6.0	7.7
Reaction Time, second	5.0	3.1
The first reaction zone	1.3	-
The second reaction zone	3.7	-
S/O	0.1	0.1
Product Slate, wt%		
Dry gas	2.88	2.95
LPG	25.69	28.08
In which propylene	8.23	9.21
Isobutane	5.96	2.18
Gasoline	43.82	40.63
LCO	12.01	11.69
HCO	7.43	8.58
Coke	8.17	7.64
Loss	-	0.43
Gasoline Octane number		
RON	91.1	92.1
MON	80.7	80.5
Gasoline Composition, wt %		
Paraffin	34.17	21.38
n-Paraffin	4.01	4.08
Iso-Paraffin	30.16	17.30
Naphthene	8.16	7.33
Olefin	28.63	45.30
Aromatics	29.04	25.99

Table 6

	Example 4	Comparative Example 3
Reactor	Multi-Cascade riser	Conventional riser
Reaction Temperature, °C		495
The first reaction zone	545	-
The second reaction zone	495	-
Reaction time, second	4.5	2.9
The first reaction zone	1.0	-
The second reaction zone	3.5	-
C/O	4.5	4.5
S/O	0.05	0.05
Product Slate, wt%		
Dry Gas	1.83	1.62
LPG	16.11	11.88
In which Isobutane	5.65	1.87
Gasoline	46.86	41.59
LCO	18.44	22.81
HCO	12.77	18.76
Coke	3.88	2.86
Loss	0.11	0.48

Table 7

	Example 4	Comparative Example 3
Reactor	Multi-Cascade Riser	Conventional Riser
Density(20°C), Kg/m <sup>3</sup>	743.6	749.8
Gasoline Octane number		
RON	90.5	91.0
MON	80.4	79.8
Induction Period, min	>1000	>485
Existent Gum, mg/100ml	2.0	2.0
Sulfur, wt%	0.0095	0.012
Nitrogen, wt%	0.0028	0.0033
C, wt%	86.14	86.81
H, wt%	13.72	13.12
Distillation, °C		
IBP	46	50
10%	73	77
30%	95	99
50%	114	122
70%	143	145
90%	171	175
EP	202	205
Composition, wt%		
Paraffins	41.01	15.81
n-paraffins	5.01	3.98
Iso-paraffins	36.00	11.83
Naphthene	7.20	6.50
Olefins	26.11	56.49
Aromatics	23.68	21.20

Table 8

Catalyst Name	A	B	B	C	D
Feedstock	80%A+ 20%C	80%A+ 20%C	D	D	D
Reaction Temperature, °C					
The first reaction zone	540	540	550	545	550
The Second reaction zone	490	490	500	495	500
Reaction time, second	3.7	3.7	5.0	5.0	5.0
The first reaction zone	1.0	1.0	1.0	1.0	1.0
The Second reaction zone	2.2	2.2	3.5	3.5	3.5
Outlet zone	0.5	0.5	0.5	0.5	0.5
C/O	3	3	5	4	6.0
S/O	0.05	0.05	0.10	0.10	0.10
Product slate, wt%					
Dry gas	0.82	0.73	2.50	2.35	2.58
LPG	9.39	11.60	23.92	19.76	22.59
In which isobutane	2.94	3.63	7.87	6.43	6.44
Gasoline	45.62	49.34	46.95	44.94	47.82
LCO	19.68	18.87	10.99	12.36	11.99
HCO	21.86	17.00	6.61	11.28	7.02
Coke	2.63	2.46	9.03	9.31	8.00
Gasoline octane number					
RON	87.4	87.3	91.0	90.6	92.1
MON	78.1	77.7	80.0	80.4	81.2
Gasoline composition, wt %					
Paraffin	43.15	45.03	42.04	43.90	37.25
n-paraffins	8.20	9.53	3.84	4.98	3.88
Iso-paraffins	34.95	36.50	38.20	38.92	33.37
Naphthene	9.86	10.03	9.26	7.33	7.16
Olefins	23.93	22.60	16.14	25.17	26.55
Aromatics	23.06	22.34	32.56	23.60	29.04
Benzene	0.45	0.41	0.41	0.60	0.70

Table 9

Operating Conditions	Example 5	Example 6
Reaction temperature, °C		
The first reaction zone	545	545
The Second reaction zone	495	495
Reaction time, second	5.3	5.3
The first reaction zone	0.8	1.1
The Second reaction zone	3.9	4.2
Outlet zone	0.6	-
C/O ratio	5.0	5.0
S/O ratio	0.05	0.05
Product Slate, wt%		
Dry gas	1.78	2.31
LPG	17.51	18.23
In which Isobutane	5.98	6.00
Gasoline	47.98	45.34
LCO	18.30	18.46
HCO	10.22	10.78
Coke	4.00	4.61
Loss	0.21	0.27



Table 10

	Example 5	Example 6
Density(20 °C), Kg/m <sup>3</sup>	745.3	746.2
Octane number		
RON	90.1	90.2
MON	80.9	80.9
Induction period, min	800.0	750.0
Existent Gum, mg/100ml	2.0	2.0
Sulfur, wt%	0.01	0.01
Nitrogen, wt%	0.003	0.003
C, wt%	86.51	86.63
H, wt%	13.42	13.32
Distillation, °C		
IBP	48	44
10%	75	71
30%	97	93
50%	118	113
70%	144	142
90%	173	170
EP	203	198
Composition, wt%		
Paraffins	47.87	37.29
n-paraffins	4.01	3.98
Iso-paraffins	43.86	33.31
Naphthene	7.45	8.03
Olefins	20.51	26.51
Aromatics	24.17	28.17

Table 11

Operating Condition	Example 7	Comparative Example 4	Example 8
Reaction Temperature, °C			
The first reaction zone	560	560	560
The Second reaction zone	510	510	510
Reaction time, second	5.3	5.0	5.3
The first reaction zone	1.0	1.0	1.0
The Second reaction zone	3.7	3.5	3.7
Outlet zone	0.6	0.5	0.6
C/O ratio			
The first reaction zone	6.0	6.0	6.0
The Second reaction zone	7.5	6.0	7.5
S/O ratio	0.1	0.1	0.1
Product slate, wt%			
Dry gas	3.24	3.01	3.34
LPG	17.33	15.15	18.43
In which isobutane	6.15	4.02	6.64
Butylenes	3.40	3.32	3.60
Gasoline	43.16	43.44	42.01
LCO	16.13	17.63	16.03
HCO	9.02	9.58	9.01
Coke	11.07	10.92	11.12
Loss	0.05	0.27	0.06
Gasoline properties			
RON	90.0	91.0	90.0
MON	80.1	79.8	80.0
Aromatics, wt%	26.87	26.35	26.82
Olefins, wt%	26.43	30.22	23.78
Paraffins, wt%	39.28	35.45	41.75
n-paraffins, wt%	4.26	4.53	4.01
Iso-paraffins, wt%	35.02	30.92	37.74
Naphthene, wt%	7.62	7.98	7.65

## 50 Claims

1. A process for catalytic conversion of hydrocarbon feedstock to produce isobutane and isoparaffin-enriched gasoline comprising

- (a) the feedstock is contacted with hot regenerated catalyst in the lower part of a reactor with the result that cracking reaction takes place;
- (b) the mixture of vapors and coke deposited catalyst is up-flowed and enters into a suitable reaction environment with the result that isomerization and hydrogen transfer reaction take place;

(c) the reaction products are separated and the spent catalyst is stripped and regenerated for recycle.

2. The process according to claim 1, wherein the catalytic cracking reaction conditions include a reaction temperature within the range of about 530 °C to 620 °C, a reaction time within the range of about 0.5 second to 2.0 seconds and a C/O ratio within the range of about 3:1 to 15:1, and hydrogen transfer reaction and isomerization reaction conditions include a reaction temperature within the range of about 420°C to 530°C, a reaction time within the range of about 2 seconds to 30.0 seconds and a C/O ratio within the range of about 3:1 to 18:1.
3. The process according to claim 2, wherein catalytic cracking reaction conditions include a reaction temperature within the range of about 550 °C to 600 °C, a reaction time within the range of about 0.8 second to 1.5 seconds, a C/O ratio within the range of about 4:1 to 12:1, and hydrogen transfer reaction and isomerization reaction conditions include a reaction temperature within the range of about 460 °C to 510 °C, a reaction time within the range of about 3 seconds to 15 seconds and a C/O ratio within the range of about 4:1 to 15:1.
4. The process according to claim 1, wherein said reactors include an iso-diameter riser, an iso-linear-velocity riser, a multi-cascade riser or a fluidized bed or a combination reactor of an iso-diameter riser and a fluidized bed.
5. The process according to claim 4, wherein said iso-diameter riser or said iso-linear-velocity riser is divided into a prelift zone, a first reaction zone where catalytic cracking reaction takes place, and a second reaction zone where hydrogen transfer reaction and isomerization reaction take place from bottom to top, and said fluidized bed is divided into a first reaction zone where catalytic cracking reaction takes place, and a second reaction zone where hydrogen transfer reaction and isomerization reaction take place from bottom to top in which the height ratio of the first reaction zone to the second reaction zone is 10~40:90~80.
6. The process according to claim 5, wherein one inlet or multi-inlets of quenching mediums is set up at the bottom of the second reaction zone and/or a heat remover is located in the second reaction zone, the height of said heat remover is about 50%~90% of the height of the second reaction zone.
7. The process according to claim 4, wherein the lower part of said combination reactor is an iso-diameter riser which serves as the first reaction zone where catalytic cracking reaction takes place, and the upper part thereof is a fluidized bed, which serves as the second reaction zone where hydrogen transfer reaction and isomerization reaction take place.
8. The process according to claim 7, wherein one inlet or multi-inlets of quenching mediums is set up at the bottom of the second reaction zone, and/or a heat remover is located in the second reaction zone, the height of said heat remover is about 50%~90% of the height of the second reaction zone.
9. The process according to claim 4, wherein the multi-cascade riser reactor with the height of from about 10 meters to about 60 meters consists of a prelift zone, a first reaction zone where catalytic cracking reaction take place, a second reaction zone with enlarged diameter where hydrogen transfer reaction and isomerization reaction take place, an outlet zone with reduced diameter from bottom to top along the coaxial direction, and the end of the outlet zone is linked to the disengager with a horizontal tube.
10. The process according to claim 9, wherein the diameter ratio of said first reaction zone to said prelift zone is about 1~2 :1 and the height of the first reaction zone is about 10%~30% of the height of the riser, and the diameter of said prelift zone is 0.02~5 meters.
11. The process according to claim 9, wherein the diameter ratio of said second reaction zone to said first reaction zone is about 1.5~5.0:1 and the height of the second reaction zone is about 30%~60% of the height of the riser.
12. The process according to claim 9, wherein the conjunct section between the first reaction zone and the second reaction zone is a circular truncated cone whose vertical section is trapezia vertex angle  $\alpha$  is generally about 30° ~ 80°, and the conjunct section between the second reaction zone and the outlet zone is a circular truncated cone, whose vertical section is trapezia base angle  $\beta$  is generally about 45° ~ 85°.
13. The process according to claim 12, wherein one inlet or multi-inlets of quenching mediums is set up at the conjunct section between the first reaction zone and the second reaction zone, and/or a heat remover is located in the second reaction zone, the height of said heat remover is about 50%~90% of the height of the second reaction zone.

14. The process according to claim 6, 8, or 13, wherein said quenching mediums are generally selected from the group consisting of quenching liquid or cooled regenerated catalyst or cooled semi-regenerated catalyst or fresh catalyst or the mixtures thereof in arbitrary ratio.

5 15. The process according to claim 14, wherein said quenching liquid is preferably selected from the group consisting of LPG, naphtha, stabilized gasoline, light cycle oil, heavy cycle oil or water or the mixtures thereof in arbitrary ratio.

16. The process according to claim 15, wherein said LPG, naphtha, and stabilized gasoline enriched olefin participate in reaction.

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17. The process according to claim 14, wherein said cooled regenerated and semi-regenerated catalysts are obtained by cooling the catalyst through catalyst cooler after primary stage and secondary stage regeneration respectively.

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18. The process according to claim 1, wherein the hydrocarbon feedstock atmospheric gas oils, naphtha, catalytic gasoline, diesel, vacuum gas oil, atmospheric residue or vacuum residue, coker gas oil, deasphalted oil, hydrotreated residue, hydrocracked residue, shale oil or the mixtures thereof.

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19. The process according to claim 1, wherein the catalysts are amorphous silica-alumina catalysts or zeolite catalysts with the active components preferably selected from the group consisting of Y, HY, USY or ZSM-5 series or any other zeolites typically employed in the cracking of hydrocarbons with or without rare earth and/or phosphor or the mixtures thereof.

20. The process according to claim 1, 14 or 17, wherein the catalysts entering into different reaction zones respectively can be of the same kind or of the different kinds.

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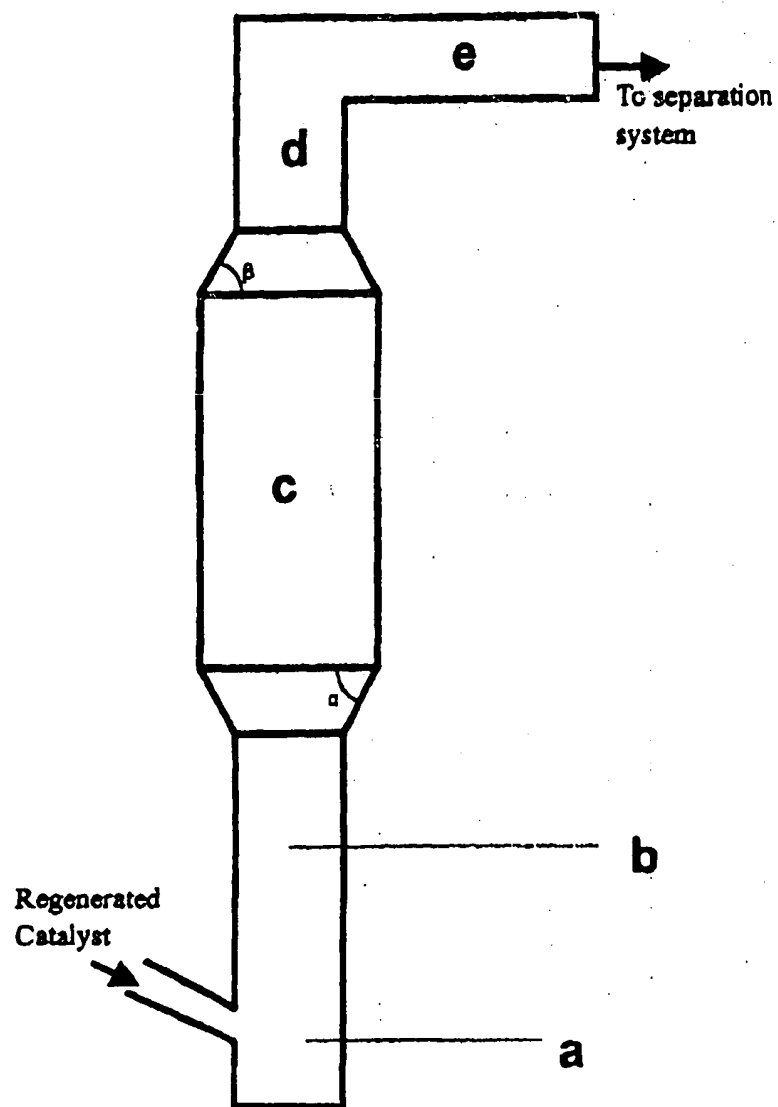


FIG. 1

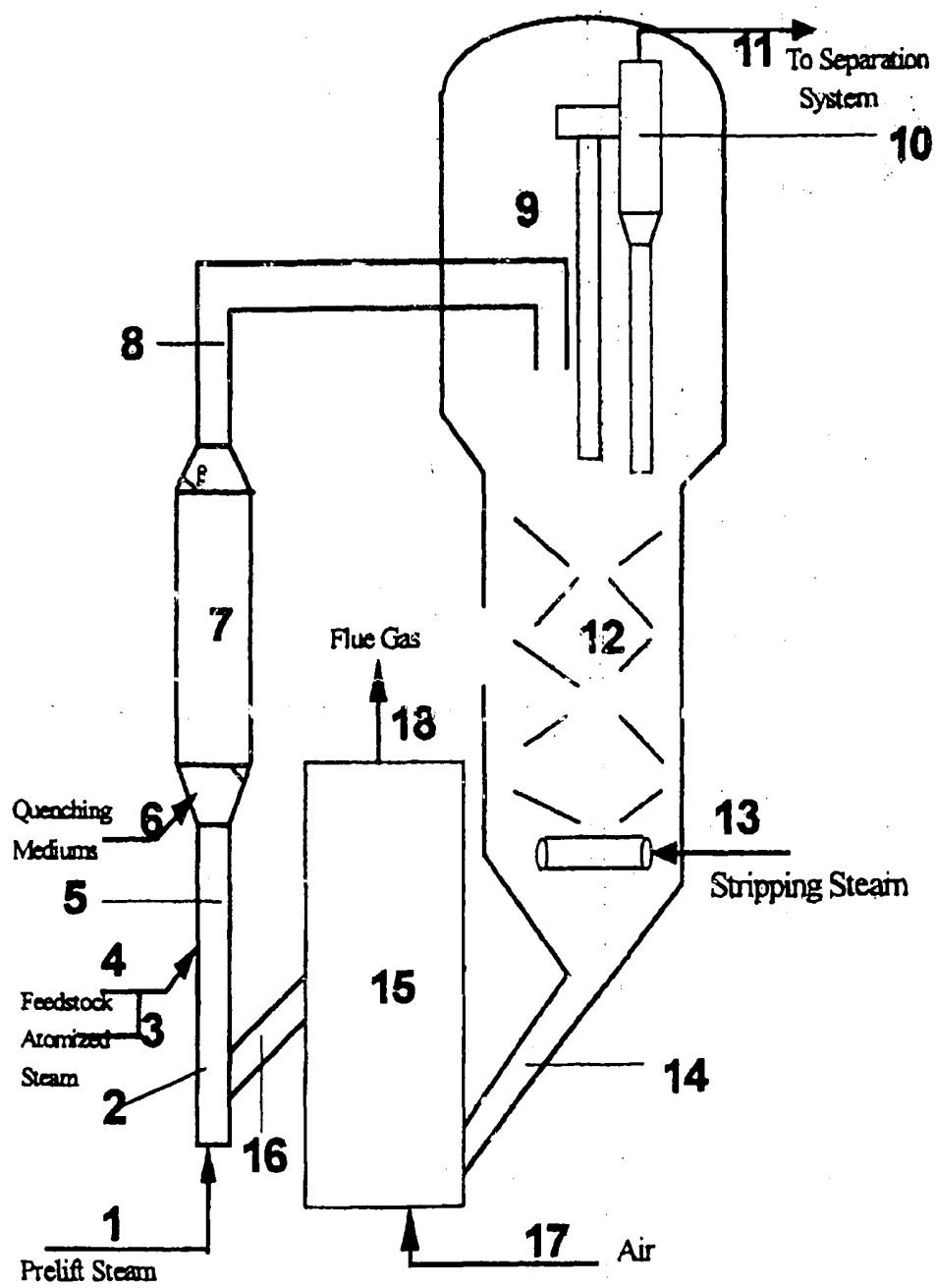


FIG. 2